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(54) Coated Solid Crop Protection Composition Formulation

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(57) Abstract		
The invention concerns agents containing one or more plant-protection substances in a formulation which is carried on a granular or pellet-form carrier and enveloped in a wax copolymer made from ethylene and an α -olefinically unsaturated monocarboxylic or dicarboxylic acid with 3 to 8 C-atoms. The invention also concerns a method of producing such agents, containing a fungicidal plant-protection substance, for the control of harmful fungi.		
(57) Zusammenfassung		
Mittel, enthaltend einen oder mehrere Pflanzenschutz-Wirkstoffe in einer Formulierung auf einem Träger und in Form eines Granulats oder als Pellets, welche mit einer Copolymerisatwachs umhüllt sind, welche aus Ethylen und einer α (ω)-olefinisch ungesättigten Mono- oder Dicarbonsäure mit 3 bis 8 C-Atomen hergestellt wurde, sowie ein Verfahren zu ihrer Herstellung und die Verwendung jener Mittel, welche als Pflanzenschutz-Wirkstoff einen fungiziden Wirkstoff enthalten, zur Bekämpfung von Schadpilzen.		

5 Coated solid crop protection composition formulation

The present invention relates to compositions containing one or more crop protection active compounds in a formulation on a carrier and in the form of granules or as pellets which are coated 10 with a copolymer wax which was prepared from ethylene and an α -olefinically unsaturated mono- or dicarboxylic acid having 3 to 8 carbon atoms, and to a process for their production and further, in the cases in which the crop protection active compound is a fungicidal active compound, to a method of controlling harmful fungi using these compositions.

It is generally known to fix crop protection active compounds to a solid carrier using coating polymers such that the active compound is only gradually released and can thus display its action 20 over a long period (slow-release formulation). The commercial products, however, have the disadvantage that they are still strongly prone to agglomeration, whereby the formulated goods lose their flowability. The relatively high content of polymer in the formulation can also be unsatisfactory.

25 It is an object of the present invention to find a formulation for crop protection active compounds which does not have these disadvantageous properties.

30 We have found that this object is achieved by compositions which contain one or more crop protection active compounds in a formulation on a carrier and in the form of granules or as pellets and which are coated with a copolymer wax which was prepared from ethylene and an α -olefinically unsaturated mono- or dicarboxylic 35 acid having 3 to 8 carbon atoms, and further, in the cases in which the crop protection active compound is a fungicidal active compound, a method of controlling harmful fungi using these compositions.

40 We have further found a process for their production and the use of those compositions which contain a fungicidal crop protection active compound for the control of harmful fungi.

Suitable crop protection active compounds are herbicidal, growth-45 regulating, insecticidal and in particular fungicidal active compounds.

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Suitable fungicidal crop protection active compounds are:

Tridemorph (2,6-dimethyl-4-tridecylmorpholine), fenpropimorph (4-(2-methyl-3-[4-tert-butylphenyl]propyl)-2,6-diethylmorpholine,
5 in particular the isomer of which, in which the methyl groups on the morpholine ring are cis to one another, fenpropidine (N-[3-(4-tert-butylphenyl)-2-methylpropyl]piperidine).

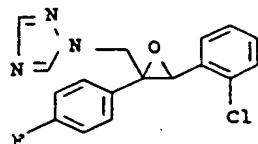
The component fenpropimorph can be present in two stereoisomeric
10 forms (morpholine ring), the cis isomer being preferred. The invention includes compositions which contain the pure isomers of the compound fenpropimorph, in particular the cis isomer, and compositions which contain mixtures of the isomers.

15 Fungicidal crop protection active compounds which are furthermore suitable are:

(+)-cis-1-(4-chlorophenyl)-2-(1H-1,2,4-triazol-1-yl)cycloheptanol, metsulfovax, cyprodinil, methyl (E)-2-(2-(6-(2-cyanophenoxy)pyrimidin-4-yloxy)phenyl)-3-methoxyacrylate and the azole active compounds N-propyl-N-[2,4,6-trichlorophenoxy]ethyl-imidazole-1-carboxamide (prochloraz), (Z)-2-(1,2,4-triazol-1-ylmethyl)-2-(4-fluorophenyl)-3-(2-chlorophenyl)oxirane (epoxiconazole) of the formula

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1-butyl-1-(2,4-dichlorophenyl)-2-(1,2,4-triazol-1-yl)ethanol
35 (hexaconazole), 1-[(2-chlorophenyl)methyl]-1-(1,1-dimethyl)-2-(1,2,4-triazol-1-ylethanol [sic], 1-(4-fluorophenyl)-1-(2-fluorophenyl)-2-(1,2,4-triazol-1-yl)ethanol (flutriafol), (RS)-4-(4-chlorophenyl)-2-phenyl-2-(1H-1,2,4-triazol-1-ylmethyl)butyronitrile, 1-[(2 RS, 4 RS; 2 RS, 4 SR)-4-bromo-40 2-(2,4-dichlorophenyl)tetrahydrofuryl]-1H-1,2,4-triazole, 3-(2,4-dichlorophenyl)-2-(1H-1,2,4-triazol-1-yl)quinazolin-4-(3H)-one, (RS)-2,2-dimethyl-3-(2-chlorobenzyl)-4-(1H-1,2,4-triazol-1-yl)-butan-3-ol, bitertanol, triadimefon, triadimenol, bromuconazole, cyproconazole, dichlobutrazole,
45 difenoconazole, uniconazole, etaconazole, fluquinconazole, imibenconazole, propiconazole, flusilazole, tebuconazole,

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imazalil, penconazole, tetraconazole, triflumizole, metconazole,
fluquinconazole [sic], fenbuconazole, triticonazole.

The fungicidal crop protection active compounds preferably originated from the group consisting of: tridemorph, fenpropimorph, fenpropidine, azole active compound, it being possible for one or more active compounds from the group consisting of tridemorph, fenpropimorph and fenpropidine to be present in the compositions.

10 The following azole active compounds are preferred: prochloraz, epoxiconazole, hexaconazole, cyproconazole, difenoconazole, propiconazole, flusilazole, diniconazole, triticonazole and tebuconazole, epoxiconazole being used with particular advantage.

15 The crop protection active compounds can also be present in the form of their salts or metal complexes. The compositions thus obtained are also included by the invention.

The salts are prepared by reaction with acids, e.g. hydrohalic acids such as hydrofluoric acid, hydrochloric acid, hydrobromic acid or hydriodic acid, or sulfuric acid, phosphoric acid, nitric acid or organic acids such as acetic acid, trifluoroacetic acid, tri-chloroacetic acid, propionic acid, glycolic acid, lactic acid, succinic acid, citric acid, benzoic acid, cinnamic acid, 25 oxalic acid, formic acid, benzenesulfonic acid, p-toluenesulfonic acid, methanesulfonic acid, salicylic acid, p-aminosalicylic acid or 1,2-naphthalenedisulfonic acid.

By choice, metal complexes can contain only one crop protection 30 active compound or alternatively several crop protection active compounds. Metal complexes can also be prepared which contain these active compounds together in a mixed complex.

Metal complexes are prepared from the organic molecule on which 35 they are based and an inorganic or organic metal salt, for example the halides, nitrates, sulfates, phosphates, acetates, trifluoroacetates, trichloroacetates, propionates, tartrates, sulfonates, salicylates or benzoates of the metals of the second main group, such as calcium and magnesium, and of the third and 40 fourth main group, such as aluminum, tin or lead, and of the first to eighth subgroup, such as chromium, manganese, iron, cobalt, nickel, copper or zinc. The subgroup elements of the 4th period and in particular copper are preferred. The metals can in this case be present in the various valencies befitting them. The 45 metal complexes can contain one or more organic molecule components as ligands.

The control of harmful fungi using the fungicidal compositions is expediently carried out by allowing a fungicidally active amount of the fungicidal composition to act in or on the soil, on the seed planted in the soil or on the plants developing therefrom or 5 on seedlings.

Owing to the delayed release of the active compounds, the release rates of the active compounds in the soil can be controlled such that, for example in the case of the fungicidal crop protection 10 active compounds, an effective protection from fungal diseases can be maintained over the whole vegetation period. Absorption of the active compound takes place continuously via the roots to the extent of the controlled release of the active compounds from the active compounds formulated according to the invention, and the 15 active compounds are then distributed in the plants systemically via the roots.

Compared with the widely used spray application of the crop protection active compounds for fungal control, the process 20 according to the invention offers the following advantages:

- Effective protection of the plants against fungal diseases can be achieved over the whole vegetation period by a single application of the active compounds formulated according to 25 the invention to soil, which advantageously is carried out together with the seed or with the planting of seedlings.
- The hitherto customary use of several spray applications to the growing crop hereby becomes unnecessary, whereby a significant expenditure of labor can be saved. 30
- By application of the crop protection active compounds in the form of the formulation according to the invention, lower amounts of the active compounds to be applied result. 35
- When using the process according to the invention, seed dressing is not necessary.

It is an essential feature of the present invention that the crop 40 protection active compounds are present in a formulation having delayed release of active compound. By means of such a controlled release of active compound, it is possible to maintain an effective protection of the crop plants against fungal attack over the entire vegetation period using one application of the fungicidal 45 compositions according to the invention to the soil.

The granules are prepared as coated granules by first applying the active compounds to solid granule-shaped carriers. The active substance-containing granules obtained are then coated with suitable coating substances which cause a delayed, controlled release 5 of active compound.

Suitable solid carriers for the coated granules are, for example, mineral earths such as silica gel, silicic acids, silica gels [sic], silicates, talc, kaolin, limestone, lime, chalk, bole, 10 loess, clay, dolomite, diatomaceous earth, calcium sulfate and magnesium sulfate, magnesium oxide, ground synthetic materials, fertilizers such as ammonium sulfate, ammonium phosphate, ammonium nitrate and ureas. e.g. crotonylidenediurea or isobutylidene-diurea, and vegetable products such as grain flour, corn flour, 15 tree bark, wood and nutshell meal, corn meal and cellulose powder. Fertilizer granules or pellets are preferred as carriers and in particular those containing phosphate.

The granules in general have a grain size range of from 0.1 to 20 10 mm, preferably from 0.5 to 8 mm, in particular from 1 to 6 mm.

The active compounds are as a rule applied to the carriers by spraying them on in the form of oil-in-water emulsions, emulsion concentrates, suspoemulsions, suspension concentrates or in 25 organic solvents, or preferably dissolved in water.

In the case of the active compounds tridemorph, fenpropimorph and fenpropidine, the use of oil-in-water emulsions, emulsion concentrates or the solutions mentioned is preferred.

30 The spraying on is carried out e.g. in fluidized bed apparatuses or in drums or rotary disks in which the carrier granules are rolled, in perforated vessels with controlled conduct of the drying medium, expediently air, or in air suspension processes. In 35 general, temperatures of from 10°C to 110°C are used for the spraying-on and the drying.

The carrier containing the applied active compound is then coated with suitable coating substances. The coating substances employed 40 for the controlled release of active compound from the coated granules are aqueous wax dispersions, containing, based on the aqueous wax dispersion, from 5 to 40% by weight of an ethylene copolymer wax, consisting of from 10 to 25% by weight of an u-definically unsaturated mono- or dicarboxylic acid having 3 to 45 8 C atoms and from 90 to 75% by weight of ethylene having an MFI value, measured at 190°C and a loading of 2.16 kp, of from 1 to 600, preferably from 5 to 500, in particular from 15 to 300, or

an MFI value, measured at 160°C and 325 p, of from 1 to 600, from 0.1 to 5% by weight of alkali metal hydroxide, ammonia, an alkanolamine or a dialkanolamine and their mixtures and, as the remainder, water to 100%.

The copolymers of ethylene to be used for the wax dispersions contain from 10 to 25, preferably from 15 to 24, % by weight of α -olefinically unsaturated mono- or dicarboxylic acids having 3 to 8 C atoms, of which, for example, acrylic acid, methacrylic acid, crotonic acid, maleic acid, fumaric acid and itaconic acid may be mentioned. Of these, methacrylic acid and, in particular, acrylic acid and their mixtures are preferred.

The ethylene copolymer waxes are characterized according to the invention by a specific MFI (melt flow index) or melt index. The MFI indicates the amount of the polymer melt in grams which can be forced at a specific temperature through a nozzle of specific dimensions with a specific expenditure of force (loading). The determination of the melt indices (MFI units) is carried out according to the following standard procedures, ASTM D 1238-65 T, ISO R 1133-1696 (E; or DIN 53 735 (1970), which are identical with one another.

The wax dispersions furthermore contain mostly bases and precisely, as a rule, from 0.1 to 5, preferably from 1 to 3, % by weight of alkali metal hydroxide, preferably potassium hydroxide or sodium hydroxide, ammonia, a mono-, di- or trialkanolamine in each case having from 2 to 18 C atoms in the hydroxyalkyl radical, preferably from 2 to 6 C atoms, or mixtures of the alkanolamines mentioned or a dialkylmonoalkanolamine in each case having from 2 to 8 C atoms in the alkyl or hydroxyalkyl radical, or their mixtures. Amines which may be mentioned are, for example, diethanolamine, triethanolamine, 2-amino-2-methylpropanol or dimethylethanolamine. Ammonia is preferably used.

Owing to the base component in the wax dispersions, the carboxylic acid groups in the copolymer waxes are at least partly present in the salt form. Preferably, these groups are neutralized to 50 to 90 and, especially, to 60 to 85%.

The coating layer can additionally contain substances for controlling the release of the active compounds. These are e.g. water-soluble substances such as polyethylene glycols, polyvinylpyrrolidone, or copolymers of polyvinylpyrrolidone and polyvinyl acetate. The amount thereof is, for example, from 0.1 to 5% by

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weight, preferably from 0.1 to 3% by weight, based on the coating substance.

The application of the coating layer is expediently carried out 5 by spraying on solutions, dispersions or dispersion [sic] of the coating substances mentioned in organic solvents or water.

An aqueous suspension or an emulsion of the coating substance is 10 preferably used which has, in particular, a content of polymer substance of from 0.1 to 50 and especially of from 1 to 35% by weight. Further auxiliaries can be added in this case to optimize the processability, eg. surface-active substances and solids such as talc and/or magnesium stearate.

15 A wax dispersion is particularly preferred which contains from 5 to 40% by weight of an ethylene copolymer wax, from 0.1 to 5% by weight of ammonia and from 55 to 94.9% by weight of water or consists of these components, the ethylene copolymer wax being composed of from 75 to 90% by weight of ethylene units and of from 20 10 to 25% by weight of units of an α -olefinically unsaturated mono- or dicarboxylic acid having 3 to 8 carbon atoms.

The coated polymers used according to the invention are generally known or obtainable according to known methods (cf. e.g. 25 DE-A 34 20 168; EP-A 201 702; US-A 5 206 279).

Spraying-on is carried out, for example, in fluidized bed apparatuses or in drums or rotating disks in which the carrier granules are rolled, in perforated vessels with controlled conduct of the 30 drying medium or in air suspension processes. In general, the process is carried out at from 10°C to 110°C.

The fungicidal compositions thus obtained and provided with the coating layer can be used as such for the control of fungi 35 according to the invention with controlled release of active compound.

However, it can also be advantageous additionally to apply active compound from outside to these compositions. The compositions 40 thus obtained enable a further graduation of the controlled release of active compound, the active compounds applied to the coating layer on the outside being important for a more specific initial action. It may additionally be advantageous also to use a second coating layer, by means of which a further possibility of 45 control for the delayed release of the active compounds results.

In addition to the coating technique described above, there is

further advantageous technique for the production of the compositions according to the invention in a formulation having delayed release of active compound in which the active compounds are incorporated into suitable matrix substances from which the active compounds are released in a delayed and controlled manner. The matrix used in this case can be, for example, the material employed for the coating. Preparation is expediently carried out here by dissolving or dispersing the active compounds in the solution or dispersion of the coating material and then applying this preparation, as described above for the coating substances, to the carrier material. It is ensured by this means that the active compounds are dispersed uniformly in the coating layer. As a rule, release from these formulations is diffusion-controlled.

15 The fungicidal compositions for example contain in general from 0.01 to 95, preferably from 0.05 to 90, % by weight of crop protection active compound.

Depending on the effect desired, the application rates are from 20 0.02 to 5 kg, preferably from 0.05 to 3 kg, of crop protection active compound per ha. The ratio of active compound in a fungicidal two-component mixture in this case is in general from 50:1 to 1:10, preferably from 20:1 to 1:5, in particular from 10:1 to 1:2.

25 The fungicidal compositions are distinguished by an outstanding activity against a broad spectrum of phytopathogenic fungi, in particular from the Ascomycetes and Basidiomycetes classes.

30 They are of particular importance for the control of a multiplicity of fungi on various crop plants such as cereals, eg. wheat, rye, barley, oats, rice, rape, sugar beet, corn, soybeans, coffee, sugar cane, decorative plants and vegetable plants such as cucumbers, beans and cucurbits. The fungicides prepared 35 according to the invention are used with particular advantage for fungal control on cereals.

The fungicidal compositions are expediently applied by allowing the composition to act in or on the soil on the seed planted in 40 the soil or on the plants developing therefrom or on seedlings. The application of the composition and the planting of the seed or the planting of the seedlings can take place in separate operations, it being possible for the application of the composition to take place before or after the planting of the seed or 45 the planting of the seedlings.

It is particularly advantageous to apply the formulated crop

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protection active compound together with the seed or the planting of the seedlings.

The following examples illustrate the invention.

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A. Examples of formulations according to the invention

10 a) The active compound epoxiconazole was processed in the form of a suspension concentrate of the following composition:

500 g/l of epoxiconazole,

15 30 g/l of a block copolymer having a propylene oxide core of approximate molecular weight 3250, to which ethylene oxide up to a molecular weight of approximately 6500 is grafted as a dispersant (BASF, Germany),

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20 g/l of a sodium salt of a condensation product of phenolsulfonic acid, urea and formaldehyde as a dispersant (BASF, Germany) and

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the difference to 1 l of water. The liquid preparations of epoxiconazole used in the following examples were obtained by diluting this suspension concentrate with the appropriate amount of water.

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b) The active compound fenpropimorph was processed as an oil-in-water emulsion of the following composition:

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200 g/l of fenpropimorph,

37 g/l of a p-isobutylphenol etherified with 8 ethylene oxide units as an emulsifier (BASF, Germany),

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87.5 g/l of a 1:1 mixture (weight) of 2-ethylhexanoic acid and a p-isobutylphenol etherified with 7 ethylene oxide units as an emulsifier (BASF, Germany) and

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the difference to 1 l of water.

1C

Example 1

a) Application of epoxiconazole to NP fertilizer

5 A solution of 3.0 g of epoxiconazole, prepared according to
(a), in 27.0 g of water were sprayed onto 4 kg of a nitrogen/
phosphate fertilizer (Nitrophoska® fertilizer 20-20-0, BASF)
with a particle size in the range 2-3.5 mm and a bulk weight
10 of 1050 g/l in a fluidized bed coating apparatus (Aromatic
coater MP 1), and the fertilizer particles obtained after
spraying were then dried. The inlet air temperature to the
fluidized bed coating apparatus was 39°C during the spraying
process and during the drying.

15 b) Application of the coating substance

The coating substance used was a wax dispersion containing
27% by weight of an ethylene/acrylic acid copolymer comprising
20% by weight of acrylic acid and 30% by weight of ethyl-
ene, 3.68% by weight of ammonia solution (25% strength by
weight), 0.20% by weight of Na₂S₂O₅ and 69.10% by weight of
water. A mixture of 740 g of this wax dispersion and 100 ml
of water was sprayed in a fluidized bed coating apparatus
onto 3.8 kg of the fertilizer granules treated with epoxi-
conazole as described in section a) above and warmed to 40°C
25 with admission of air at from 39 to 42°C over a period of
70 min. Drying was then carried out at from 39 to 42°C for a
further 10 min with further admission of air. The content of
30 the coating layer in the coated fertilizer granules obtained
after drying was 5% by weight, based on the coated fertilizer
granules.

Example 2

35 The procedure was as described in Example 1b), but 4.89 kg of the
wax dispersion were sprayed as a coating substance onto 12 kg of
the fertilizer granules treated with epoxiconazole as described
in Example 1a) at an air inlet and air outlet temperature in the
range 45-48°C, the total time for the spraying and drying being
40 175 min. The content of the coating layer, based on the coated
fertilizer granules obtained after drying, was 10% by weight.

Example 3

45 The procedure was as described in Example 1b), but three times
the amount of the wax dispersion were sprayed on at an air inlet
and air outlet temperature of 44-45°C, the total time for the

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spraying and the subsequent drying being 200 min. The content of the coated layer, based on the coated fertilizer granules obtained after drying, was 15% by weight.

5 Example 4

a) Application of fenpropimorph to NP fertilizer

10 20 g of fenpropimorph (according to (β), see above) were sprayed in the course of about 11 min at an air inlet temperature of 60°C onto 4 kg of a nitrogen/phosphate fertilizer (Nitrophoska® fertilizer 20-20-0 NASF) having a particle size in the range 2-3.5 mm in a fluidized bed coating apparatus (Aeromatic coater MP 1).

15 b) Application of the coating substance

20 The coating substance used was a wax dispersion containing 27% by weight of an ethylene/acrylic acid copolymer comprising 20% by weight of acrylic acid and 80% by weight of ethylene, 3.68% by weight of ammonia solution (25% strength by weight), 0.20% by weight of Na₂S₂O₅ and 69.10% by weight of water. A mixture of 713 g of this wax dispersion and 96 ml of water was sprayed in a fluidized bed coating apparatus onto 25 2.8 kg of the fertilizer granules treated with fenpropimorph (according to (β), see above) and warmed to 45°C with admission of air at from 40 to 42°C over a period of 62 min. Drying was then carried out for a further 5 min with further admission of air at from 40 to 42°C. The content of the coating 30 layer in the coated fertilizer granules obtained after drying was about 5% by weight, based on the coated fertilizer granules.

Example 5

35 The procedure was as described in Example 4b), but, as a coating substance, 1.428 kg of the wax dispersion were sprayed onto 3.4 kg of the fertilizer granules treated with fenpropimorph as described in Example 4a) at an air inlet and air outlet 40 temperature in the range 44-45°C, the total time for the spraying and subsequent drying being 125 min. The content of the coating layer, based on the coated fertilizer granules obtained after drying, was about 10% by weight.

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Example 6

The procedure was as described in Example 4b), but 2.142 kg of the wax dispersion were sprayed onto 3.4 kg of the fertilizer granules treated with fenpropimorph as described in Example 4a) at an air inlet and air outlet temperature of 44-45°C, the total time for the spraying and the subsequent drying being 190 min. The content of the coating layer, based on the coated fertilizer granules obtained after drying, was 15% by weight.

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Example 7

Corresponding to Examples 1a) and 4a), two active compound solutions were applied by two separate nozzles to 3.8 kg of NP 20-20-0 fertilizer granules simultaneously. One solution contained 2.5 g of epoxiconazole (according to (a), see above) and the other an oil-in-water emulsion of 15 g of fenpropimorph. After drying, the granules treated in this way were treated corresponding to the spraying procedure 1b) or 4b) with 740 g of the wax dispersion described there, the air inlet temperature being 45°C and the total time for the application 62 min.

Example 8

25 15 g of fenpropimorph were stirred as such into and uniformly dispersed in 740 g of the wax dispersion described in Example 1b). Using this preparation, 3.8 kg of NP 20-20-0 fertilizer granules were coated as in Ex. 1b) (45°C air inlet temperature, 52 min application time).

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Example 9

The procedure was as in Example 8, only instead of 15 g of fenpropimorph 2.5 g of epoxiconazole (according to (a), see above) 35 were stirred in as such.

Example 10

The procedure was as in Example 8, only in addition to the 15 g 40 of fenpropimorph 2.5 g of epoxiconazole (according to (a), see above) were also stirred as such into the wax dispersion.

Examples 11 - 16

45 Examples 11 - 16 were carried out in a similar manner to Examples 1, 2, 4, 5 and 7 in each case using 3.8 kg of NP 20-20-0 fertilizer granules, but instead of the wax dispersion described above

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using an aqueous polymer dispersion (of the type Acronal®, BASF) which consisted to 60% by weight of water and to 40% by weight of a copolymer of methyl methacrylate and n-butyl acrylate (1:1) as coating substance. The individual application rates and test parameters can be seen from the following table. The inlet air temperature in all cases was 40 - 45°C.

	Ex.No.	Fenpropimorph as pure substance [g]	Epoxyconazole according to (a) [g]	Acronal (40% strength)	Time for spraying
10	11	15	-	500 g	43 min
	12	15	-	1000 g	~2 min
	13	-	2.5	500 g	43 min
	14	-	2.5	1000 g	82 min
	15	15	2.5	500 g	49 min
	16	15	2.5	1000 g	87 min

20 The amount of coating in the finished granules was 5% by weight each in Examples 11, 13 and 15, and 10% by weight each in Examples 12, 14 and 16. The product was subsequently also powdered on a disk with 0.25% by weight of talc.

25 Examples 17 - 22

Examples 17 - 22 were carried out in a similar manner to Examples 11 - 16, but the active compounds were not applied separately but were stirred into the coating dispersion used and then applied together with this. The application rates and the other process parameters remained virtually unchanged.

Examples 23 and 24

35 Examples 23 and 24 were carried out in a similar manner to Examples 11 and 13, but the carrier material used was 2.0 kg of pumice split having a particle size of 2.0 - 3.5 mm and a bulk weight of 430 g/l. On account of the lower density of the pumice split, the coating amount in the finished product was in this case 10% by weight.

Examples 25 - 30

40 Examples 25 - 30 correspond in their implementation to the examples described above as follows: Example 25 corresponds to Example 11, Example 26 corresponds to Example 17, Example 27 corresponds to Example 13, Example 28 corresponds to Example 19,

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Example 29 corresponds to Example 15 and Example 30 corresponds to Example 21. Instead of the 3.8 kg of NP 20-20-0 fertilizer, however, 1.8 kg of corn meal (product of Eurama S.A. (France) of the type Eu-Grit 8/10) having a particle size of 2.0 - 3.15 mm and a bulk weight of 450 g/l was used as the carrier material. The amount of coating substance was also 10% by weight here because of the lower bulk weight. The air inlet temperature was 50°C and the time for spraying from 40 to 50 min. The finished granules were also treated with 1% by weight of talc.

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Example 31

Corresponding to Example 7, solutions of 7.5 g of fenpropimorph (according to (β), see above) and of 1.25 g of epoxiconazole (according to (α), see above) in 38.75 g of water were first applied to 3.8 kg of NP 20-20-0 fertilizer and dried. A mixture of 500 g of the Acronal dispersion described in Examples 11 - 16, 5 g of fenpropimorph (according to (β), see above) and 0.83 g of epoxiconazole (according to (α), see above) was then applied as a coating and dried (time: 45 min, temp.: 45°C inlet air). Finally, solutions of 2.5 g of fenpropimorph (according to (β), see above) in 10.8 g of water and 0.42 g of epoxiconazole (according to (α), see above) were again applied to the coating on the outside. The finished product contains 5% by weight of coating material and half of the active compounds are dispersed under the coating, a third in the coating matrix and a sixth on the outside on the coating.

Example 32

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This example was carried out in a similar manner to Example 31, but instead of the Acronal dispersion 740 g of the wax dispersion described in Example 1b) were used (time: 55 min, temp.: 50°C). The product contained 5% by weight of coating material and has the active compound distribution shown in Example 31.

Example 33

The example was carried out in a similar manner to Example 31. However, the individual application rates of the active compounds were varied such that their distribution in the finished product changed such that one third of the active compounds were applied under the coating and two thirds were embedded in the coating material.

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Example 34

This example was carried out in a similar manner to Example 33, but 740 g of the wax dispersion as described in Example 1b were used as coating material.

This example was carried out in a similar manner to Examples 31 and 33, but instead of the fertilizer 1.8 kg of corn meal as described in Examples 25 - 30 were used as carrier granules.
10 Because of the lower bulk weight, in this case a coating amount of 10% by weight again resulted in the finished product. Active compound dispersion was carried out by applying two thirds under the coating layer and embedding one third in the coating layer.

15 B. Use examples

Testing of the fungicide granules having delayed release of active compound for the control of seed- and airborne harmful fungi on cereals

20 Fungicide granules having delayed release of active compound were mixed with winter wheat seed of the variety Rektor such that during simultaneous sowing of 200 kg/ha of loose smut- and covered smut-infected wheat and [sic] 100 kg/ha of the fungicide granules
25 according to the invention were applied to the same drill row using a drilling machine. The amounts of active compound were, per ha, 300 g of fenpropimorph or 50 g of epoxiconazole or, on combination of both active compounds, 125 g of fenpropimorph and 25 g of epoxiconazole (Use Example 1). On complete ripening of
30 the wheat (development stage 89), the cobs attacked by loose smut (*Ustilago tritici*) and covered smut (*Tilletia caries*) were counted and the effectiveness of the fungicide granules was converted to efficiencies according to Abbott (0 = without effect, 100 = harmful fungus completely controlled). The results are
35 shown in Use Example 1.

The application of seed and granules was also carried out with barley seed of the variety Beate and the fungicide granules having delayed release of active compound in the same manner as with
40 the wheat seed. 200 kg/ha of barley and 200 kg/ha of the fungicide granules according to the invention were sown simultaneously. The amount of active compound per ha was 750 g of fenpropimorph or 125 g of epoxiconazole or, in combination, 375 g of fenpropimorph and 125 g of epoxiconazole (Use Example 2). At
45 the end of the barley blooming period (development stage 69), attack by mildew (*Erysiphe graminis*) and net blotch (*Pyrenophora teres*) was determined as total plant attack and the effect of the

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fungicide granules was converted into efficiencies according to
Abbott. Use Example 2 shows the results of this test.

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Use Example 1
 Control of seed-borne loose smut (*Ustilago tritici*) and covered smut (*Tilletia caries*) on wheat in the open using coated granules based on a nitrogen/phosphate fertilizer (NP fertilizer) and the fungicidal active compounds fenpropimorph and epoxiconazole by root absorption

Treatment	Type of granules	Application rates of fungicidal active compound g/ha	Control of the smut diseases	
			Potency according to Abbott 0 - 100 determination date complete ripening of the wheat	<i>Ustilago tritici</i> <i>Tilletia caries</i>
Control without granules	-	-	0	0
NP fertilizer	without coating	-	0	0
NP fertilizer	wax dispersion coating according to Ex. 1b)	-	0	0
NP fertilizer	wax dispersion coating + fenpropimorph	300	90	66
NP fertilizer	wax dispersion coating + epoxiconazole	50	100	100
NP fertilizer	wax dispersion coating + epoxiconazole + fenpropimorph	125 25	100	100

The results show that fenpropimorph and epoxiconazole applied in the form of slow-release granules absorbed by the plant roots achieved efficiencies of 66-100 and thus can be designated as good to very good control methods.

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Use Example 2
 Control of mildew (*Erysiphe graminis*) and net blotch (*Pyrenophora teres*) on barley in the open using
 coated granules based on a nitrogen/phosphate fertilizer (NP fertilizer) and the fungicidal active
 compound fenpropimorph and epoxiconazole by root absorption

Treatment	Type of granules	Application rates of fungicidal active compound g/ha	Control of the smut diseases Potency according to Abbott 0 - 100 Determination date complete ripening of the wheat [sic] <i>Ustilago tritici</i> [sic] <i>Tilletia caries</i> [sic]
Control without granules	-	-	0
NP fertilizer	without coating	-	0
NP fertilizer	polymer coating according to Example 11	-	0
NP fertilizer	polymer coating + fenpropimorph	750	86
NP fertilizer	polymer coating + epoxiconazole	125	57
NP fertilizer	polymer coating + epoxiconazole + fenpropimorph	375 125	100 91

It emerges from the table that fenpropimorph and epoxiconazole applied in the form of slow-release granules control the airborne causative agents *Erysiphe graminis* and *Pyrenophora teres* even on absorption via the plant roots. The combination of both active compounds in this method achieves the highest efficiencies.

Annex: New claims

1. A composition, composed essentially of a granule- or pellet-shaped carrier treated with one or more crop protection active compounds and of a coating which for its part consists essentially of a copolymer wax which is composed of from 75 to 90% by weight of ethylene and from 10 to 25% by weight of an α -olefinically unsaturated mono- or dicarboxylic acid having 3 to 8 carbon atoms, the copolymer wax having an MFI value of 1 to 600, measured at 160°C and 325 p [sic], and it being possible for the mono- or dicarboxylic acid to be present completely or partially in the form of salts with alkali metal ions, ammonium ions or identical or different alkanolammonium ions as cations.
2. A composition as claimed in claim 1, which comprises, as crop protection active compounds, fungicidal crop protection active compounds.
3. A composition as claimed in claim 2, wherein the fungicidal crop protection active compounds are tridemorph and/or fenpropimorph and/or fenpropidone as well as a further fungicidal crop protection active compound.
4. A composition as claimed in claim 3, wherein the further crop protection active compound is an azole active compound.
5. A composition as claimed in claim 4, wherein the azole active compound is selected from the following group: prochloraz, epoxiconazole, hexaconazole, cyproconazole, difenoconazole, propiconazole, flusilazole, tebuconazole, diniconazole, tritriconazole.
6. A composition as claimed in any of claims 1 to 5, wherein the granule- or pellet-shaped carrier is a fertilizer.
7. A composition as claimed in claim 6, wherein the fertilizer contains phosphate.
8. A process for preparing the composition as claimed in any of claims 1 to 7, wherein the copolymer wax is applied to the granule- or pellet-shaped carrier treated with one or more crop protection active compounds in the form of a wax dispersion which contains from 5 to 40% by weight of the copolymer wax.

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9. A process as claimed in claim 8, wherein, as wax dispersion,
an aqueous suspension or a water emulsion of the copolymer
wax is used.

5 10. A method of controlling fungi, which comprises allowing a
fungicidally active amount of a composition as claimed in any
of claims 1 to 7 to act in or on the soil on the seed planted
in the soil or the plants developing therefrom or on
seedlings.

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